

PATENT SPECIFICATION

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(54) ELECTROSTATIC IMAGE TONER COMPOSITIONS

(71) We, EASTMAN KODAK COMPANY, a Company organised under the laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrography and to a particulate toner composition and a dry electrographic developer composition containing such a toner useful in the development of latent electrostatic charge images.

Electrographic imaging and developing processes, e.g. electrophotographic imaging processes and techniques, have been extensively described in both the patent and other literature. Generally these processes have in common the steps of forming a latent electrostatic charge image on the surface of an insulating electrographic material. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the electrographic material is brought into contact with a suitable developer mix which deposits particles on the charged or the uncharged areas. Conventional dry developer mixes include toner or marking particles and may also include a carrier vehicle for the toner that can be either a magnetic material such as iron filings, powdered iron or iron oxide, or a triboelectrically chargeable, non-magnetic substance like glass beads or crystals of inorganic salts such as sodium or potassium fluoride. The toner or marking particles typically contain a resinous material suitably coloured or darkened, for contrast purposes, with a colorant such as dyestuffs or pigments such as carbon black.

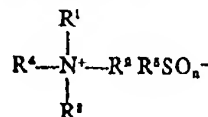
One method for applying a suitable dry developer mix to a charged image-bearing electrographic material is by the well-known magnetic brush process. Such a process may also use an apparatus of the type described, for example, in U.S. Patent No. 3,003,462 and customarily comprises a non-magnetic rotat-

ably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in or otherwise contacted with a supply of developer mix consisting of magnetically attractable carrier particles and pigmented toner particles which adhere to the surface of the carrier particles.

In magnetic brush development, as well as in various other types of electrographic development wherein a dry triboelectric mixture of a particulate carrier vehicle and a toner powder are utilized, e.g., cascade development such as described in U.S. Patents 2,638,416 and 2,618,552, it is advantageous to modify the triboelectric properties of the toner powder so that a uniform, stable relatively high net electrical charge may be imparted to the toner powder by the particulate carrier vehicle. It is also highly advantageous if the triboelectric properties of the toner powder remain fairly uniform even when the toner powder is used under widely varying ambient relative humidity (RH) conditions.

A variety of methods for modifying the triboelectric properties of particulate toner particles have been proposed including the addition of various compounds as 'charge control agents'.

According to the present invention there is provided a dry particulate electrostatic image toner powder consisting of particles having a size from 0.1 to 100 microns comprising a polymeric binder having a softening point, measured as herein defined, in the range 40°C to 200°C, optionally a colorant, and containing from 0.01 to 2 per cent by weight of the toner particles of a charge control agent having the formula:



in which R¹, R², R³ and R⁴, which may represent the same or different groups, repre-

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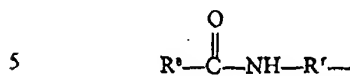
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sent an aliphatic or aromatic group having up to 30 carbon atoms, providing that at least one of the groups R¹, R², R³ and R⁴ has the structure:



in which Rⁿ is an alkyl group having eight or more carbon atoms and R' is a straight-chain alkylene group having up to eight carbon atoms, Rⁿ is an aliphatic or aromatic group having up to 30 carbon atoms and n is 3 or 4. Preferably Rⁿ is an aromatic group having 6 to 10 carbon atoms.

There are also provided electrostatic image developers comprising carrier particles having a size from 30 to 1200 microns and toner particles according to the invention.

The present invention has been found to provide numerous advantages. Among others, the charge control agents used in the invention have been found to provide a dry, particulate toner composition which exhibits a relatively high, uniform and stable net toner charge when admixed with a suitable particulate carrier vehicle. Moreover, the amount of deleterious toner throw-off is generally quite low. In addition, the charge control agents used in the invention have been found to have no deleterious effect on the adhesion properties of the resultant toner composition containing these charge control agents when such toner compositions are used to conventional plain paper receiving sheets.

In addition to the foregoing advantages, the charge control agents used in the present invention have been found even more effective at providing a resultant electrostatic toner composition which is capable of maintaining a relatively high, stable net toner charge level (when admixed with a particulate carrier vehicle under widely varying relative humidity (RH) conditions) than certain, somewhat similar prior art charge control agents, i.e. the short-chain (non-surfactant) quaternary ammonium salts described in U.K. Patent Specification No. 1,420,839 and U.S. Patent No. 3,893,935. This is particularly advantageous as it permits one to obtain effective electrographic development with low amounts of toner throw-off even at relatively low and high RH conditions, for example, 5% RH at 28°C and 90% RH at 28°C.

It has further been found that toner particles containing an effective amount of the above-described charge control agents generally result in good to excellent electrographic developed images exhibiting good uniform density with little or no background scumming.

The polymers useful as binders in the practice of the present invention include those polymers and resins conventionally employed

in electrostatic toners. Useful polymers generally have a glass transition temperature within the range of from 40° to 120°C. Preferably, toner particles prepared from these polymeric materials have relatively high caking temperature, for example, higher than 55°C, so that the toner powders may be stored for relatively long periods of time at fairly high temperatures without having individual particles agglomerate and clump together. The softening temperature of useful polymers preferably is within the range of from 40°C to 200°C so that the toner particles can readily be fused to conventional paper receiving sheets to form a permanent image. Especially preferred polymers are those having a softening temperature within the range of from 40°C to 65°C because toners containing these binders can be used in high-speed electrographic copy machines using plain paper as the receiving sheet to which the toned images are fused.

As used herein the term "softening temperature" refers to the softening temperature of the polymer as measured by an E. I. duPont de Nemours Company, Model 941 TMA (Thermal Mechanical Analyzer). Glass transition temperature (T_g) as used herein refers to the temperature at which a polymeric material changes from a glassy polymer to a rubbery polymer. This temperature (T_g) can be measured by differential thermal analysis as disclosed in *Techniques and Methods of Polymer Evaluation*, Vol. 1, Marcel Dekker, Inc., N.Y. 1966.

Among the various polymers which may be used in the toner particles of the present invention are styrene-containing resins, polycarbonates, rosin modified maleic alkyd resins, polyamides, phenol-formaldehyde resins and various derivatives thereof, polyester condensates, modified alkyd resins, aromatic resins containing alternating methylene and aromatic units such as described in U.S. Patent No. 3,809,554, and fusible cross-linked polymers as described in U.K. Patent Specification No. 1,477,504 and U.S. Patent 3,938,992.

Especially useful toner polymers include certain polycarbonates such as those described in U.S. Patent No. 3,694,359 and which include polycarbonate materials containing an alkylidene diarylene portion in a recurring unit and having up to 10 carbon atoms in the alkyl portion. Other useful polymers having the above-described physical properties include polymeric esters of acrylic and methacrylic acid such as poly(alkylacrylate) including poly(alkylmethacrylate) wherein the alkyl portion can contain up to 10 carbon atoms. Additionally, other polyesters having the aforementioned physical properties are also useful.

Still other especially useful toner polymers are various styrene-containing resins. Such polymers typically comprise a polymerized

blend of from 40 to 100 percent by weight of styrene, including styrene homologue; from up to 45 percent by weight of one or more lower alkyl acrylates or methacrylates, i.e. having up to 4 carbon atoms in the alkyl portion such as methyl, ethyl, isopropyl and butyl, and up to 50 percent by weight of one or more vinyl monomers other than styrene, for example, a higher alkyl acrylate or methacrylate (including branched alkyl and cycloalkyl acrylates and methacrylates), having from 6 to 20 or more carbon atoms in the alkyl group. A typical styrene-containing polymer prepared from a copolymerized blend as described hereinabove are copolymers prepared from a monomeric blend of 40 to 60 percent by weight styrene or styrene homologue, from 20 to 50 percent by weight of the lower alkyl acrylate or methacrylate and from 5 to 30 percent by weight of the higher alkyl acrylate or methacrylate such as ethylhexyl acrylate. Especially useful styrene-containing binder resins are cross-linked fusible styrene-containing polymers such as described in the above-referenced Belgian Patent 817,748. A variety of other useful styrene containing toner materials are disclosed in the following U.S. Patents: 2,917,460; 2,788,288; 2,638,416; 2,618,552 and 2,659,670 and U.S. Reissue Patent 25,136.

The amount of binder polymer employed in the toner particles used in the present invention may vary depending on the amounts of other addenda which one may desire to incorporate in the toner composition. For example, various colorant and/or magnetic materials can advantageously be incorporated in the toner particles when the particles are desired for use in certain applications requiring such addenda. Typically, however, the binder polymer is present in an amount equal to or greater than 50 percent by weight of the toner composition. And, in accord with certain particularly useful embodiments of the invention where it is desired to employ the resultant toner composition in a high speed electrographic office copy machine, it is desirable to use an amount of binder polymer within the range of from 75 to 98 weight percent based on the total weight of the particulate toner composition.

The toner particles of the present invention can be prepared by various methods. One convenient technique for preparing these toners is spray-drying. Spray-drying involves dissolving the binder polymer and adding the toner colorant and charge control agent to a volatile organic solvent such as dichloromethane. This solution is then sprayed through an atomizing nozzle using a substantially non-reactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent evaporates from the airborne droplets, producing toner particles of the uniformly dyed or pigmented resin. The ultimate

particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Particles of a diameter between 0.1 and 100 microns may be used; although, in general, present day office copy devices typically employ particles between 1.0 and 30 microns. However, larger particles or small particles can be used where desired for particular methods of development or particular development conditions.

Another convenient method for preparing the toner composition of the present invention is melt-blending. This technique involves melting a powdered form of toner polymer or resin and mixing it with suitable colorants, such as dyes or pigments, and the charge control agent. The polymer can readily be melted on heated compounding rolls which are also useful to stir or otherwise blend the polymer and addenda so as to promote the complete intermixing of these various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant solid mass is then broken into small particles and finely ground to form a free-flowing powder of toner particles. These particles typically have an average particle size within the range of from 0.1 to 100 microns.

As described hereinabove the charge control agents used in the invention are added to the polymeric toner composition in an amount effective to improve the charge properties of the toner composition. The addition of a charge control agent improves the charge uniformity of a particular toner composition, i.e. acts to provide a toner composition in which all or substantially all of the individual discrete toner particles exhibit a triboelectric charge of the same sign (negative or positive) with respect to a given carrier vehicle, increases the net electrical charge exhibited by a specified quantity of toner particles relative to a given carrier vehicle, and reduces the amount of "toner throw-off" of a given toner composition. As used herein, the phrases "net electrical charge exhibited by a toner powder" or "net toner charge" are equivalent and are defined as the total electrical charge exhibited by a specified amount of a particular carrier vehicle. Although the phenomenon by which such an electrical charge is imparted is not fully understood, it is believed due in large part to the triboelectric effect caused by the physical admixture of toner and carrier. As used herein, the term "toner throw-off" is defined as the amount of toner powder thrown out of a developer mix as it mechanically agitated, e.g., in a development apparatus. Aside from the extraneous contamination problems inherent with airborne toner dust in the development apparatus, "toner throw-off" also leads to imaging problems such as un-

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wanted background and scumming of the electrographic image-bearing element.

The amount of the charge control agent useful in the present invention is important.

5 The amount of charge control agent used lies within the range of from 0.01 to 2 weight percent and preferably 0.2 to 1.5 weight percent based on the total weight of the particulate toner composition. It has been found that
10 if amounts much lower than those specified above are used, the charge control agent tends to exhibit little or substantially no improvement in the properties of the toner composition. As amounts more than 1.5 weight
15 percent of the charge control agent are used, especially amounts more than 2.0 weight percent, it has been found that the net toner charge exhibited by the resultant toner composition becomes quite unstable and is substantially reduced. Of course, it must be
20 recognized that the optimum amount of charge control agent to be added will depend in part on the particular charge control agent selected and the particular toner composition to which it is added. However, the amount specified hereinabove is the useful range of
25 charge control agent of the present invention which can be effectively used in conventional dry toner materials.

30 In accord with one useful embodiment of the invention, it has been found that the charge control agents used in the invention tend to provide the best results when the concentration of the charge control agent within an individual toner particle is greater at
35 or near the surface of the particle than it is within the interior of the particle. Of course, useful results can also be obtained in accord with the present invention when the charge control agents described herein are distributed in a uniform manner throughout the
40 toner particle composition.

More specifically, the quaternary ammonium compounds used in the present invention have
45 been found to exhibit excellent charge control characteristics even at very low relative humidities, e.g. 15% RH or less. In contrast, the somewhat related short-chain, non-surfactant quaternary ammonium salt charge control agents described in U.K. Patent Specification 1,420,839 and U.S. Patent 3,893,935,
50 although useful, do not provide nearly as effective charge control characteristics as is obtained by the charge control agents of the present invention at low relative humidities.

55 This is shown with reference to the accompanying drawings in which Figure 1 is a graph showing the relationship between net toner charge, in microcoulombs per gram, and the relative humidity at 28°C for two developers. Figure 2 is a graph showing the relationship between the net toner charge and number of simulated prints produced on an electrophotographic copier for two developers.
60 Further description of the methods by which

these graphs were obtained is given in Examples 1 and 4 herein.

It will be shown that at low relative humidities, a toner composition containing a non-surfactant charge control agent, exhibits
70 increasingly higher charge levels such that the toner composition quickly acquires a charge level outside of a useful magnetic brush developer charge range of 8 to 35 microcoulombs/gram as compared with
75 developers containing toner particles according to the invention. Of course, it will be appreciated that the useful charge range of a given type of electrostatic developer may vary depending, for example, upon whether
80 one is using a cascade or magnetic brush developer, and even upon the specific developer system, e.g. one roll or two roll magnetic brush, with which one is working. In any case, however, the significant aspect
85 of the relationship shown in Figure 1 is that it clearly shows that with toner particles containing the prior art short-chain, non-surfactant quaternary ammonium salt charge control agents, one can quickly reach a point under
90 low, relative humidity conditions at which the toner particles are charged to an unacceptably high charge level. Toner particles exhibiting such a high charge tend to become so tightly bound, through electrostatic forces, to the
95 carrier particles with which they are associated that it becomes extremely difficult to separate these toner particles from the carrier particles and into contact with the electrostatic images to be developed.

100 As indicated, various organo-sulphur-containing groups may be used as the anionic groups useful in the charge agents of invention. Typically, such groups contain up to
105 10 carbon atoms including such anions as alkyl sulphates and sulphonates, such as methyl sulphate and methane sulphonate and aryl sulphonates, such as p-toluene sulphonates.

A variety of colorant materials selected
110 from dyestuffs or pigments may be used alone or in combination in the toner materials of the present invention. Such materials serve to colour the toner and/or render it more visible. Of course, suitable toner materials
115 having the appropriate charging characteristics can be prepared without the use of a colorant material where it is desired to have a developed image of low optical opacity. In those instances where it is desired to
120 utilize a colorant, the colorants used can, in principle, be selected from virtually any of the compounds mentioned in the *Colour Index* Volumes 1 and 2, Second Edition.

125 Included among the vast number of useful colorants would be such materials as Hansa Yellow G (C.I. 11680), Nigrosine Spirit soluble (C.I. 50415), Chromagen Black BTOO (C.I. 45170), Solvent Black 3 (C.I. 26150), Fuchsine N (C.I. 42510), C.I. Basic
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Blue 9 (C.I. 52015), etc. Carbon black also provides a useful colorant. The amount of colorant or colorant mixture added may vary over a wide range, for example, from 1 to 20 percent of the weight of the polymeric binder. Particularly good results are obtained when the amount is from 2 to 10 percent. In certain instances, it may be desirable to omit the colorant, in which case the lower limit of concentration would be zero.

The toners of this invention can be mixed with a carrier vehicle to form developing compositions. The carrier vehicles which can be used with the present toners to form new developer compositions can be selected from a variety of materials. Suitable carrier vehicles useful in the invention include various non-magnetic particles such as glass beads, crystals of inorganic salts such as sodium or potassium chloride, hard resin particles and metal particles.

In addition, magnetic carrier particles can be used in accordance with the invention. In fact, the toner compositions of the present invention are especially suited for use with magnetic carrier particles as the problem of "toner throw-off" is especially bothersome in magnetic brush development processes. Suitable magnetic carrier particles are particles of ferromagnetic materials such as iron, cobalt, nickel, and alloys and mixtures thereof. Other useful magnetic carriers are mixtures of rough-surfaced, irregularly-shaped magnetic particles and smooth-surfaced, regularly-shaped magnetic particles such as described in U.S. Patent No. 3,838,054. Other useful magnetic carriers are particles wherein each individual carrier particle contains a plurality of magnetic particles uniformly dispersed throughout an electrically insulating polymeric matrix such as described in Canadian Patent 835,317. Other useful magnetic carriers are ferromagnetic particles overcoated with a thin layer of various film-forming resins, for example, the alkali-soluble carboxylated polymers described in U.S. Patent 3,547,822. Still other useful resin coated magnetic carrier particles are described in U.S. Patent 3,632,512; U.S. Patent No. 3,795,617 and U.S. Patent No. 3,795,618. Other useful resin coated magnetic carrier particles include carrier particles coated with various fluorocarbons such as poly-tetrafluoroethylene, polyvinylidene fluoride, and mixtures thereof including copolymers of vinylidene fluoride and tetrafluoroethylene.

A typical developer composition containing the above described toner and a carrier vehicle generally comprises from 1 to 10 percent by weight of particulate toner particles. Typically, the carrier particles are larger than the toner particles. Conventional carrier particles have a particle size on the order of from 30 to 1200 microns, preferably 60-300 microns.

The toner and developer compositions of this invention can be used in a variety of ways to develop electrostatic charge patterns or latent images. Such developable charge patterns can be prepared by a number of means and be carried for example, on the insulating light sensitive photoconductive layer of an electrophotographic material or a non-light sensitive dielectric-surfaced element such as a receiver sheet. One suitable development technique involves cascading the developer composition across the electrostatic charge pattern; while another technique involves applying toner particles from a magnetic brush. This latter technique involves the use of a magnetically attractable carrier vehicle in forming the developer composition. After imagewise deposition of the toner particles, the image can be fixed by heating the toner to cause it to fuse to the substrate carrying the toner. If desired, the unfixed image can be transferred to another support such as a blank sheet of copy paper and then fixed to form a permanent image.

The following examples are included for a further understanding of the invention.

Example 1

In this example a charge control agent of the present invention was compared to tetrapentylammonium chloride, the highly useful charge control agent described in U.K. Patent Specification 1,420,839.

Toner A (prior art)

100 parts poly(styrene - co - methyl methacrylate - co - ethylhexyl methacrylate) —polymeric binder
0.5 parts Tetrapentylammonium chloride—charge control agent
5 parts 'Regal' 300 R the trade mark of a carbon black purchased from Cabot Corp.—colorant

Toner B (present invention)

100 parts poly(styrene - co - methyl methacrylate - co - ethylhexyl methacrylate) —polymeric binder
0.5 parts (3 - lauramidopropyl)trimethylammonium methyl sulfate—charge control agent
5 parts 'Regal' 300R carbon black—colorant

Toners A and B were prepared by melt blending the addenda on a 2-roll mill, cooling the material, and then grinding in a fluid energy mill to an average size of from 3 to 15 microns.

In the melt-blending preparation of both Toners A and B, the colorant and charge agent were added in an identical manner during the melt-blending operation. Upon analysis of the Toner A composition, it was found that the concentration of the charge control agent in Toner A at or near the

exterior surface of the Toner A particles was equivalent to that which one would expect assuming the charge agent was dispersed in a uniform manner throughout the Toner A particle composition during melt blending. However, upon analysis of the composition of Toner B, it was found that the concentration of the charge agent in Toner B at or near the exterior surface of the Toner B particles was much greater than the aforementioned concentration of charge agent found at or near the surface of the Toner A particles.

Toners A and B were employed in a magnetic brush developer mix containing 3 weight percent toner and 97 percent by weight of magnetic carrier particles composed of 'Hocganaes' EH sponge iron particles (average particle size 125 microns) partially coated with a fluorocarbon resin. The developer mixes containing Toners A and B were

labelled Developer A and Developer B, respectively.

The effective charge ($\mu\text{coul/gram}$) of these developers was measured at various levels of relative humidity and the results of these measurements are shown in Figure 1. It will be noted that in a useful triboelectric charge range of 8—35 $\mu\text{coul/gram}$, Developer B (containing the charge control agent of the present invention) is operable at a wider range of relative humidities than is Developer A.

Example 2

In this example, Developer A and Developer B (as described in Ex. 1) were separately tumbled for 15 minutes and their triboelectric charge measured. The developers were then allowed to rest undisturbed for 3 days and their charge again measured. The results are given in Table I:

TABLE I

Developer	Charge After Tumbling 15 Minutes ($\mu\text{coul/gram}$)	Charge After 3 Days ($\mu\text{coul/gram}$)	% Charge Decay
A (Prior Art)	29.6	22.9	-23%
B (Present Invention)	22.2	19.7	-11%

Table I shows that the charge decay of Developer B is significantly lower than that of Developer A. Minimal charge decay is important for a developer mix used in an electrographic copier to obtain uniform initial print quality upon start-up of the copier after shutting down for an extended period, such as a weekend.

Example 3

Two charge control agents were tested with a Thermo Gravimetric Analyzer (TGA) to determine their decomposition temperature. The results are given in Table II:

TABLE II

Charge Control Agent	Decomposition Temperature ($^{\circ}\text{C}$)
Tetrapentylammonium Chloride (prior art)	181
(3-lauramidopropyl)tri- methylammonium methyl sulfate (present invention)	279

Table II shows that the above-noted charge control agent suitable for use in the toner compositions of the present invention has a higher decomposition temperature than the prior art tetrapentylammonium chloride. This higher decomposition temperature eliminates degradation problems during compounding of the charge agent into the toner.

Example 4

Two toners of the following composition were prepared in a manner similar to Example 1:

Toner C (present invention)

100 parts styrene-containing polymeric binder
0.5 parts (3 - lauramidopropyl)trimethyl-
ammonium methyl sulphate
5 parts 'Regal' 300 R carbon black

Toner D (prior art)

100 parts styrene-containing polymeric binder
5 parts 'Regal' 300R carbon black

Toners C and D were used at 3 weight percent concentration in a magnetic brush developer mix as described in Example 1. These developers were then put through a simulated 30,000 print run in an electro-photographic copier. The data, see Figure 2, indicates that Developer "C" containing the charge control agent of the present invention would be electrically stable over this period, but that the prior art Developer "D" would not.

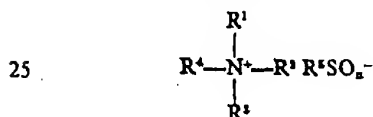
Example 5

A number of dry toner formulations were prepared as in Example 1 in order to define the effective concentration range of the subject charge agent. These toner formulations

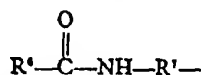
represented a concentration series using (3-lauramidopropyl) - trimethylammonium methyl sulphate, a representative charge control agent of the present invention, at levels varying from 0 to 2 parts by weight based on 100 parts by weight polymeric binder contained in the toner formulations. The toner particle formulations were prepared and tested for charge and throw-off characteristics. The data indicated that the preferred concentration range is approximately 0.2 to 1.5 parts equivalent to approximately 0.2 to 1.5 per cent by weight of charge agent based on the total weight of the toner formulations.

WHAT WE CLAIM IS:—

1. A dry particulate electrostatic image toner powder consisting of particles having a size from 0.1 to 100 microns comprising a polymeric binder having a softening point, measured as herein defined, in the range 40°C to 200°C, optionally a colorant, and containing from 0.01 to 2 per cent by weight of the toner particles of a charge control agent having the formula



in which R^1 , R^2 , R^3 and R^4 , which may represent the same or different groups, represent an aliphatic or aromatic group having up to 30 carbon atoms, providing that at least one of the groups R^1 , R^2 , R^3 and R^4 has the structure:



in which R^5 is an alkyl group having eight or more carbon atoms and R^6 is a straight-chain alkylene group having up to eight carbon atoms, R^5 is an aliphatic or aromatic group having up to 30 carbon atoms and n is 3 or 4.

2. The dry particulate electrostatic image toner powder as claimed in Claim 1 in which the group R^1 is an alkyl group having up to ten carbon atoms.

3. The dry particulate electrostatic image toner powder as claimed in Claim 2 in which the charge control agent is (3 - lauramidopropyl) - trimethyl ammonium methyl sulphate.

4. The dry particulate electrostatic image

toner powder as claimed in Claims 1 or 2 in which the group R^1 is an aromatic group having 6 to 10 carbon atoms.

5. The dry particulate electrostatic image toner powder as claimed in any of the preceding Claims in which the polymeric binder is a styrene-containing resin.

6. The dry particulate electrostatic image toner powder as claimed in any of the preceding Claims in which the polymeric binder contains one or more pigments or dyestuffs as a colorant.

7. The dry particulate electrostatic image toner powder as claimed in Claim 6 in which the polymeric binder contains carbon black.

8. The dry particulate electrostatic image toner powder as claimed in any of the preceding Claims in which the charge control agent is present in an amount from 0.2 to 1.5 per cent by weight of the particles.

9. Dry particulate electrostatic image toner powder as claimed in Claim 1 and as herein described.

10. An electrostatic image developer comprising carrier particles having a size from 30 to 1200 microns and from 1 to 10 per cent by weight of dry particulate toner particles as claimed in any of the Claims 1 to 9.

11. The electrostatic image developer as claimed in Claim 10 in which the carrier particles have a size from 60 to 300 microns.

12. The electrostatic image developer as claimed in Claims 10 or 11 in which the carrier particles are magnetically attractable.

13. Electrostatic image developer as claimed in Claim 10 and as herein described.

14. The method of forming an image comprising treating a surface bearing an electrostatic charge image with an electrostatic image developer as claimed in any of the Claims 10 to 13 to deposit a toner image thereon.

15. The method as claimed in Claim 14 wherein the surface bearing the electrostatic charge is that of an insulating photoconductive layer.

16. The method as claimed in Claim 14 or 15 wherein the deposited toner image is transferred to a receiving sheet.

17. Methods of forming toner images as claimed in Claims 14, 15 and 16 and as herein described.

18. Image bearing surfaces whenever prepared by the method of any of the Claims 14 to 16.

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